ESTER FUELS VIA NON-AQUEOUS ENZYME-CATALYZED REACTIONS OF FATTY ACIDS

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ABSTRACT

The use of nonaqueous enzyme slurries for the production of fatty ester fuels from coal-derived alcohols and fatty acids was investigated. Phenolic tars from coal gasification wastes were fractionated and treated with ethylene oxide to convert them to an alcohol, and the intermediate alcohols were esterified with the fatty acids in a nonaqueous lipase system. Lipases in a variety of organic solvents were investigated for acylation of coal-derived alcohols. The two step process transformed the black poorly soluble phenolics to clean paraffin-soluble esters. Diesel testing demonstrated that the phenoxyethyl esters could be substituted for diesel fuels.

INTRODUCTION

The production of diesel fuels from vegetable oils by conversion of the triglyceride to a less viscous ester has been extensively investigated. Most of the focus has been on methyl and ethyl esters, because of the ease of preparation and the low cost of methanol. Coal-derived alcohols may represent another inexpensive alcohol source for forming the ester diesel fuel. Phenolic materials are produced in large amounts during coal conversion processing to coke, liquids, or synthesis gas. Coal gasification produces a crude phenol/cresol stream from extraction of the condensate water. At the Great Plains Gasification plant operated by Dakota Gasification Company, the Phenosolvan extraction process recovers about 97 million pounds per year of the crude phenolics (1). The phenolics can be esterified with acid chlorides and anhydrides, but not with the less inexpensive esters or acids.

Alcohols can be produced from coal liquefaction and gasification byproduct phenolics by reaction of the phenolic hydroxyl groups with epoxides to give phenoxyalkanols. The hydroxyethylated and hydroxypropylated phenolics undergo esterification reactions at the alcohol group with esters and acids that do not occur readily with the original phenolic group.

Non-aqueous enzyme systems can greatly facilitate many organic reactions, especially those that result in formation of esters and amides. We previously reported the application of non-aqueous enzyme slurries to the production of fatty ester fuels from coal-derived alcohols (2,3). Most of our earlier work utilized triglyceride substrates as the acyl source for transesterification or interesterification reactions of these alcohols. But some inexpensive fatty acids are available form sources such as tall soaps and wastes from vegetable oil processing.

In order to develop an economical process for production of alternative ester fuels, a study of lipase-catalyzed reactions of fatty acids was carried out in nonaqueous solvents. The goal of this work was to exploit the advantage that enzymes in nonaqueous solvents can offer by driving the equilibrium toward the ester products. This paper will discuss the conversion of phenolic materials from coal gasification byproduct streams to a diesel fuel by using enzyme-catalyzed esterification reactions.

EXPERIMENTAL

Hydroxyethylated phenolics

The hydroxyethylation of the Great Plains crude phenols with ethylene oxide or other reagents was previously discussed (2,3). The composition of the hydroxyethylated intermediate was determined to be as follows: 2-phenoxyethanol, 45%; 2-(2'-methylphenoxyethanol, 10%; 2-(3-and 4-methylphenoxy)ethanol, 23%; other alkylphenoxyethanols 22%.

Acylation of hydroxyethylated phenolics

Hydroxyethylated Great Plain phenols (0.300 g) were reacted with 0.600 g of oleic acid in a slurry containing 100 mg Amano PS-30 lipase in 15 ml of solvent at 65°C. The reaction was allowed to proceed for 20 hrs. The product mixture was centrifuged to separate the enzyme, and the reaction mixture was analyzed by GC.

RESULTS AND DISCUSSION

The crude phenolic stream from the Great Plains Gasification Plant was reacted with ethylene oxide to give a hydroxyethylated intermediate (2). The lipase-catalyzed esterification reaction of the hydroxyethylated phenolics with equimolar amounts of oleic acid (free acid form) was found to give a high yield of the oleate ester in hexane solvent. With the Amano PS-30 lipase, a conversion of 83% to oleate ester was achieved for both the phenoxyethanol and the methylphenoxyethanol components of the intermediate. The corresponding transesterification conversions obtained using triglyceride substrates (tripalmitin, canola oil) were 90-95% (3), but these transesterification reactions used an excess of the triglyceride to drive the reaction. The reaction of oleic acid was repeated on a large batch to verify the high yield of ester product. The same yield of ester was obtained.

The reaction of 2-phenoxyethanol (the major component of the hydroxyethylated phenolic mixture) with oleic acid was further investigated with Amano PS lipase and with porcine pancreatic lipase in various solvents to determine the role of the organic solvent in the reaction. Yields of the phenoxyethyl ester product from oleic acid utilizing Amano PS lipase as a slurry phase in various organic solvents are reported in Table 1. The high yield of ester in the nonpolar hydrocarbon solvents may be attributed to formation of reverse micelles of unreacted fatty acid that can trap the water byproduct so that the reverse reaction (hydrolysis) does not occur at a fast rate. The reverse micelles do not form in the polar solvents, and the water is miscible and able to participate in the hydrolysis (reverse) reaction. Thus, the esterification reaction can be effectively driven to high conversion only in a nonpolar solvent. An excess of the fatty acid could probably give even higher yields by driving the equilibrium to the right, but this was not investigated, since an excess of fatty acid is not desirable in the fuel product. An extra step might then be required for removal of unreacted fatty acid.

The high conversion found for toluene as the solvent contrast significantly with the results obtained earlier for the transesterification with triglyceride. In these earlier studies with canola oil, use of toluene as the solvent resulted in poor conversions to the ester. The low transesterification reactivity in toluene has not been adequately explained. Hexane is a good solvent for both esterification and transesterification, however.

An additional tactic for shifting the equilibrium and thereby increasing the conversion to ester is the removal of product water from the reaction by the addition of molecular sieves. Several attempts were made to increase the ester yields for the reaction of phenoxyethanol and hydroxyethylated Great Plains phenols by adding molecular sieves to the bacterial lipase slurry. These experiments gave low yields of ester, unfortunately. The molecular sieve may have efficiently absorbed the water byproduct and then effectively catalyzed the hydrolysis reaction, overcoming the enzyme-catalyzed esterification. Also the molecular sieve may have removed the essential water associated with the enzyme protein, resulting in conformation changes that deactivated the enzyme.

The lipase-catalyzed reaction of the potassium salt (soap) of oleic acid was also investigated, since soaps are the form of tall acid byproduct obtained directly from the Kraft process. The reaction was carried out in chloroform. It was hoped that the metal ion would be carried along in the micellar form. The reaction gave no ester product, however. Possibly the carboxylate form of the acid was not acceptable at the lipase active site.

The direct esterification reaction of oleic acid with 2-phenoxyethanol was also investigated with porcine pancreatic lipase but poor yields (1-6%) of ester were obtained with this enzyme even in the nonpolar solvents. In contrast, good yields were obtained in earlier studies of transesterification with this lipase. The reason for the inactivity of the pancreatic enzyme in esterification reactions has not been determined. The esterification results with the Amano AK lipase obtained from a different Pseudomonas strain paralleled the lower rates found for this enzyme in other catalytic reactions.

Another set of experiments was carried out to determine the extent to which the lipases are deactivated by the gasification byproduct derivatives. The samples contain small amounts of soluble black materials that are not easily removed by distillation, adsorption, or solvent extraction. These are possibly condensation products of dihydroxybenzenes and indoles or other nitrogen heterocyclics. Accumulation of these impurities at the enzyme sites might be responsible for considerable shortening the lifetime of a enzyme catalyst bed. Earlier

experience with coals, humates, and low-severity liquefaction products from several coals showed that the lipases are substantially inhibited by many coal-derived materials (1).

The series of reactions carried out with recovered enzymes demonstrated that significant deactivation of the enzyme occurred. In a series of four reactions, the activity decreased by 20% in each successive reaction. The enzymes recovered from the fourth reaction were washed with acetone to determine whether substances that deactivated the enzyme could be removed by a more polar solvent or were instead bound reversibly. Reaction of the acetone-washed enzymes in the same system as above resulted in no ester formation initially. However, it was known from previous work that acetone removes essential water from the bacterial lipases, converting them to an inactive form. Thus, a small amount of water was added back to the enzymes which were then used for oleic acid esterification. The ester yield from the rehydrated or regenerated lipase was 25%, demonstrating partial restoration of the activity.

In previous studies with triglycerides, enzyme deactivation of the lipase was observed, but only to 3 to 10% of the original activity. Thus, there may be some kind of synergistic inhibitory effect involving the free fatty acid forms and the inhibitors present in the hydroxyethylated GP phenol intermediate.

Ester fuel prepared by acylation of hydroxyethylated GP phenols with canola oil exhibited a viscosity of 32.8 centipoise. This is substantially higher than that of sunflower methyl ester or #2 diesel oil. A 1:1 mixture of the ester product with #2 diesel gave acceptable viscosity (12.2 centipoise). Diesel tests with the mixture showed ignition delays (1.97 ms) that were slightly longer than the #2 diesel (1.84), but pressure curves were virtually identical.

CONCLUSIONS

Lipase-catalyzed reactions of inexpensive fatty acids with coal-derived alcohols in hydrocarbon solvents gave high yields of ester products. The high conversion of the acid form is very interesting, since it means that the very poorest grades of vegetable oils and the byproducts from their refining can be used in the preparation of esters. These oils contain high concentrations of the fatty acids. Raw tall oil from the Kraft pulping process also contains high concentrations of fatty acids. Much of the tall soap has no market and is mostly burned on site for heating the black liquor for recovering sulfide. Tall fatty acids are mainly oleic and linoleic acid.

The enzyme-deactivation results demonstrate that the impure hydroxyethylated phenolic streams cannot be effectively utilized without purification to remove the inhibitory compounds prior to the enzymatic reactions. Thus, the use of cleaner alcohols (from fermentation or Fischer-Tropsch) offer a better possibility for lipase-catalyzed fatty acid esterification. Alternatively, acid-catalyzed reactions in nonpolar solvents might give high enough yields of paraffin-soluble esters for use in diesel engines.

ACKNOWLEDGEMENTS

The support of the U.S. Department of Energy SBIR Contract # DE-AC02-88ER80614 is gratefully acknowledged.

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Table 1. Yields of 2-phenoxyethyl oleate from Amano PS 30 lipase-catalyzed reaction of oleic acid with 2-phenoxyethanol (55°C for 24 hrs).

Test	Solvent	% Yield
1	Hexane	86
2	Toluene	86
3	Acetone	24
4	THF	0